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(54) Title: CATALYST SYSTEMS FOR POLYCONDENSATION REACTIONS

(57) Abstract: The invention pertains to new catalyst systems for polycondensation reactions, for example for producing polyethylene terephthalate. In accordance with the invention, complex compounds with hydrotalcite-analogous structures of general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{n+}(A^{n-})_n \cdot mH_2O$ are used, wherein M(II) represents divalent metals, preferably Mg or Zn or Ni or Cu or Fe(II) or Co, and M(III) represents trivalent metals, for example Al or Fe(III), and A represents anions, preferably carbonates or borates. These catalysts can be calcinated and can be used in combination with phosphorus compounds that contain at least one hydrolyzable phosphorus-oxygen bond.



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CATALYST SYSTEMS FOR POLYCONDENSATION REACTIONS

The invention pertains to new catalyst systems for polycondensation reactions.

5 The synthesis of polyesters, for example polyethylene terephthalate, requires the use of catalysts in the polycondensation step. The literature contains an abundance of patents describing the use of various catalytically active substances. Today especially antimony and titanium compounds are used on a large industrial scale in the manufacturing of polyethylene terephthalate. This is also reflected in the large number of patents that
10 describe the use of such compounds. Polyester-soluble antimony compounds are described in US Patents 3,965,071; 3,998,793; 4,039,515; 4,116,942; 4,133,800; 4,454,312; 5,750,635; and 5,780,575 as polycondensation catalysts. Modified antimony derivatives (stabilization by substances with double bonds to prevent reduction to metallic antimony) are, for example, subjects of Patents US 4,067,856; US 4,067,857; and US 4,130,552.
15 Antimony salts of trimellitic acid esters are likewise used as catalysts in the manufacturing of polyethylene terephthalate (US 5,478,796). Titanium derivatives, especially tetraalkyl titanates, are protected in the Patents US 4,039,515; US 4,131,601; US 4,482,700; US 5,066,766; US 5,302,690; WO 97/45470; and US 5,744,571. A combination of sulfonic acid, titanate and antimony (or germanium) compound is the subject of US Patent 5,905,136.
20 Germanium compounds are also described as catalysts for the polycondensation reaction (US 5,378,796; US 5,830,981; US 5,837,786; and US 5,837,800). Catalytically active compounds in a polycondensation reaction are likewise borates and acetates of zinc, calcium, cobalt, lead, cadmium, lithium, or sodium (US 4,115,371).

Defined silicon compounds (2-cyanoethyltriethoxysilane and 3-
25 aminopropyltriethoxysilane) are protected in a US Patent (US 4,077,944) as polycondensation catalysts.

The combination of several metal compounds is described in the following patents: US 4,080,317 (Sb/Pb/Zn, Sb/Pb/Ca, Sb/Zn, Sb/Pb/Mg, Sb/Pb/Ca/Mn, Sb/Pb/Ca/Zn, Sb/Pb/Li, Sb/Mn, Ti/Ca, Ge/Ga, Ge/Zn, and Ge/K); US 4,104,263 (Sb(Zr)/Zn(Ca,Mn)); US
30 4,122,107 (Sb/Zn(Ca,Mn)); US 4,356,299, US 4,501,878, and US 5,286,836 (Ti/Sb); US 4,361,694 (Ti/Si); US 4,468,489 (Ti,Zr,Ge,Zn); US 4,499,226 and US 5,019,640 (Sb/Co); US 5,008,230 (Co(Zn)/Zn(Mn,Mg,Ca)/Sb); US 5,138,024 and US 5,340,909 (Zn/Sb); US 5,565,545 and US 5,644,019 (Sb/Ge); US 5,596,069 (Co/Al); US 5,608,032 and US

5,623,047 (Sb/Co(Mg,Zn,Mn,Pb)); US 5,656,221 (Sb/Co/Mn); US 5,714,570 (Sb/Ti/Zn); and US 5,902,873 (Ti(Zr)/lanthanide). At least one constituent of these complex catalysts is a "classical" polycondensation catalyst, either antimony, titanium, or germanium.

Finely dispersed titanates are the subject of US Patent 5,656,716. Jointly
5 precipitated titanium and silicon compounds and titanium and zirconium compounds are described in US Patents 5,684,116 and 5,789,528.

A polycondensation catalyst on the basis of zeolites (alkali or alkaline earth metal-modified aluminosilicate) is protected in US Patent 5,733,969. The use of titanium compounds leads to yellowing of the polyester produced during polycondensation and
10 processing. Especially during the use of polyethylene terephthalate as a food packaging, this color is undesirable.

The use of antimony as a catalyst is permitted only within precisely established boundaries, since this substance, as a heavy metal, is physiologically problematic.

The goal of this invention is to discover a catalyst system for the
15 polycondensation, especially of polyethylene terephthalate, polybutylene terephthalate, or polytrimethylene terephthalate, which is physiologically safe and makes it possible to use the polycondensation products for food packaging. In terms of catalytic activity in polycondensation and selectivity, it must be compatible with conventional catalysts and must not influence the processing properties of polyester at all or only to the desired degree.

20 Quite surprisingly, it was found that complex compounds with hydrotalcite-analogous structures of the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{**}(A^{n-})_{xn}.mH_2O$, (the use of which was previously described only as a filler (US 5,362,457; US 5,225,115; JP 09 077,962; JP 02 308,848; JP 61 118,457; JP 56 059,864), in olefin isomerizations, as an adsorbents (halogen trapper), as a carrier material for catalysts, flame retardant, molecular
25 sieve, anion exchanger and catalyst for alcohol reactions (isophorone synthesis), hydrogenations, polymerizations, and reforming reactions (F. Cavani, F. Trifiro, A. Vaccari, *Catalysis Today* 11 (1991), 173-301)), before or after calcination, alone or in combination with phosphorus compounds that contain at least one hydrolyzable phosphorus-oxygen compound, are excellently suited for catalysis of polycondensation reactions, especially for
30 the production of polyalkylene terephthalate.

In the formula mentioned, M(II) represents divalent metals, preferably Mg or Zn or Ni or Cu or Fe(II) or Co, and M(III) represents trivalent metals, preferably Al and Fe, and A represents anions, preferably carbonates or borates or titanil compounds.

The particle size of the hydrotalcite used falls in the range of 0.1 to 50 μm ,
5 preferably 0.5 to 5 μm .

The calcination of the hydrotalcites can be performed at temperatures of 200°C to 800°C, preferably at 400°C to 650°C.

As phosphorus compounds which contain at least one hydrolyzable phosphorus-oxygen bond, phosphoric acid esters or esters of phosphorous acid can be used.

10 The catalyst system in accordance with the invention is used in the concentration ratio of hydrotalcite to phosphorus compound of 1:0.5 to 1:4, preferably 1:1 to 1:2.

The untreated or the calcinated hydrotalcite-analogous derivatives in combination with phosphorus compounds as stabilizers with at least one hydrolyzable
15 phosphorus-oxygen bond show increased catalytic activity and selectivity in comparison to conventional catalysts and are characterized by high food compatibility.

It has been found that these substances, made up of several components, are highly catalytically selective, relatively independent of their composition, although the individual constituents catalyze polycondensation reactions either not at all or only with a
20 very low selectivity and thus generate a high fraction of byproducts. It was also found that with the targeted selection of the constituents, surprisingly it was possible to influence the applications properties of the polyesters, for example the crystallization behavior. The polycondensation with the catalyst system in accordance with the invention is carried out under vacuum in a liquid phase at temperatures of 230°C to 280°C or in a solid phase at
25 temperatures of 170 to 240°C.

The addition of phosphorus compounds with at least one hydrolyzable phosphorus-oxygen bond leads to improved thermal stability of the polyesters, especially in the industrially required long residence times of the liquid polyesters under normal pressure in comparison to polyesters produced with conventional [catalysts], for example with
30 catalysts on the basis of antimony and titanium compounds, but also in comparison to products produced under hydrotalcite catalysis.

Through the combination of hydrotalcite-analogous compound/stabilizer, molecular weight degradation and discoloration of the polyester can be lowered significantly without a negative influence on other important processing properties of the polyester, for example the crystallization behavior and the clarity of the final product.

5 In the following, the invention will be explained on the basis of exemplified embodiments.

In a 250-ml, single-necked flask with agitator and distillation attachment, 100 g precondensate of terephthalic acid and ethylene glycol with an average molecular weight was placed together with the catalyst. This apparatus was evacuated to about 0.5 mbar and
10 purged with nitrogen. This process was repeated a total of three times. The glass flask was dipped into a hot salt bath at 280°C and the precondensate allowed to melt at this temperature. As soon as the melting was complete, vacuum was carefully applied.

Following termination of the polycondensation by purging with nitrogen, the product was allowed to cool in the flask, and the polyester was characterized according to its
15 separation from the adhering glass.

The intrinsic viscosity (IV) was determined on an apparatus from the Schott Company (AVSPro) of 250 mg resin dissolved in 50 ml phenol/dichlorobenzene (1:1).

DSC measurements were performed on a Perkin-Elmer DSC 7.

The acetaldehyde determination took place according to the following
20 procedure:

The PET material was precooled in liquid nitrogen and ground in an ultracentrifuge mill. The ground material was immediately weighed into a headspace vial and closed gas-tight with a septum. After holding a constant quantity of gas at 150°C for 90 minutes in the headspace sampler, the gas was injected onto the GC column, at a defined
25 pressure. The color numbers were determined with a LUCI 100 spectrophotometer from the Lange Company.

Table 1 contains characteristic values of polyesters that were obtained by polycondensation reactions at temperatures of 280°C using various hydrotalcite catalysts.

Table 1. Characterization of polyethylene terephthalate from polycondensation reactions with various untreated or calcinated hydrotalcite-analogous derivatives

Experiment no.	Catalyst	Concentration (ppm)	Reaction time (minutes)	IV (dl/g)	Acetaldehyde (ppm)	T _g ¹ (°C)	T _c ² (°C)	T _{cc} ³ (°C)	T _m ⁴ (°C)
1 (comparison example)	Antimony (III) acetate	350	180	0.7480	14.2	79.7	198.9	163.2	248.6
2 (example in acc. with the invention)	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	100	180	0.5648	14.4	78.9	197.1	143.5	254.3
3 (example in acc. with the invention)	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	250	165	0.7350	20.7	81.5	184	153.5	251.7
4 (example in acc. with the invention)	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	500	150	0.6862	16.7	80.9	183.2	150.8	250.1
5 (example in acc. with the invention)	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	1000	150	0.8412	17.4	82.5	179.3	154.2	252.9
6 (example in acc. with the invention)	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720)	1000	90	0.8893	44	84.1	175.2	153.5	252.3
7 (example in acc. with the invention)	Zn ₄ Al ₂ (OH) ₁₀ CO ₃ ·H ₂ O calcinated (18 hours, 450°C)	500	180	0.6932	16.4	81.9	185.3	152.8	254.4

Table 1 - Continued. Characterization of polyethylene terephthalate from polycondensation reactions with various untreated or calcinated hydrotalcite-analogous derivatives

8*(example in acc. with the invention)	$\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	500	210	0.6617	22.2	85.2	207.2		251.6
9*(example in acc. with the invention)	$\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	1000	150	0.7704	19.7	79.3	198.4	144	249.6
10*(example in acc. with the invention)	$\text{Mg}_3\text{ZnAl}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	1000	165	0.6302	17.3	79.6	189.4	153.5	254.3
11*(example in acc. with the invention)	$\text{Mg}_2\text{Zn}_2\text{Al}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	1000	180	0.7031	17.3	82.5	201.8	136.1	251.6
12*(example in acc. with the invention)	$\text{MgZn}_3\text{Al}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	1000	120	0.7608	20.2	84.3	201.1	138.1	255.1
13*(example in acc. with the invention)	$\text{Zn}_4\text{Al}_2(\text{OH})_{12}(\text{B}_3\text{O}_3(\text{OH})_4)_2^*$ H ₂ O calcinated (18 hours, 450°C)	1000	135	0.8362	22.8	83.3	200.8	137.4	251.7

*The specification for producing the catalyst tested in this example can be found in: A. Bhattacharyya, D.B. Hall: Materials Synthesis and Characterization, 1997, 139-145.

¹Glass temperature; ²crystallization temperature; ³cold crystallization; ⁴melting point.

Table 1 clearly shows that all tested untreated or calcinated hydrotalcite-analogous derivatives have catalytic activity. The synthesized polyethylene terephthalate, depending on the catalyst used, has different processing-related properties.

5 An additional important criterion for assessing the suitability of untreated or calcinated hydrotalcite-analogous derivatives is their catalytic activity in so-called solid state polymerization (SSP).

For these experiments, six of the polyesters listed in Table 1 were subjected to SSP. For this purpose the products were left for 96 hours at 200°C in a vacuum drying oven. After cooling, characteristic values relevant for applications technology were
10 determined.

The results of solid state polymerizations of polyethylene terephthalate are summarized in Table 2.

Table 2. Polyesters from solid state polymerization

No.	Catalyst	Concentration (ppm)	IV (dl/g) after polycondensation	IV (dl/g) after SSP	Acetaldehyde (ppm)	T _g (°C)	T ₀ (°C)	T _{ec} (°C)	T _m (°C)
1	Zn ₆ Al ₂ (OH) ₁₆ CO ₃ ·H ₂ O calcinated (18 hours, 450°C)	500	0.6932	1.1891	0.3	84.1	162.8	166.9	249.6
2	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	100	0.5648	0.7755	0.4	82.2	178.6	156.1	253
3	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	250	0.7350	0.9549	0.4	83.9	172.9	161.5	253
4	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	500	0.6862	1.0775	0.3	83.1	166.2	161.5	249.6
5	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720); calcinated (18 hours, 450°C)	1000	0.8412	1.1005	0.3	84.4	170.9	162.8	252.3
6	Al-Mg-hydrotalcite (acc. to US Patent 5,437,720)	1000	0.8893	1.301	0.9	84.6	176.7	155.5	253.2
7	Mg ₄ Al ₂ (OH) ₁₂ (B ₃ O ₃ (OH) ₄) ₂ ·H ₂ O O calcinated (18 hours, 450°C)	500	0.6617	0.8509	0.6	83.5	201.4	140.8	253.0
8	Mg ₃ Al ₂ (OH) ₁₂ (B ₃ O ₃ (OH) ₄) ₂ ·H ₂ O O calcinated (18 hours, 450°C)	1000	0.6302	0.8009	0.6	82.7	179.2	161.5	254.4

Table 2 shows the fundamental suitability of the untreated or calcinated hydrotalcite-analogous derivatives as catalysts for polycondensation reactions in both liquid and solid phase.

It is especially important that it is possible by selecting the constituents of these complex catalysts to systematically influence the process technology properties of the polyester resins, for example the crystallization behavior.

The use of the hydrotalcite catalysts in accordance with the invention in combination with phosphorous compounds which contain at least one hydrolyzable phosphorus-oxygen bond is described in the examples that follow.

Example 14 (Comparison Example)

In a 200 liter reactor of alloyed steel, a suspension of 60.675 kg terephthalic acid and 1.44 kg isophthalic acid were placed in 31.6 kg ethylene glycol. Under agitation, this reaction mixture was treated with 45.5 g antimony triacetate and 8.125 g cobalt acetate tetrahydrate in 1000 g ethylene glycol, and 34.65 g tetramethylammonium hydroxide in 500 g ethylene glycol. The closed reactor was heated to 272°C. At 2.8 bar the slow expansion of the pressurized container was started. After about 20 minutes under normal pressure, 12 g phosphoric acid in 500 g ethylene glycol were added. Then the liquid phase polymerization was started by slow application of the vacuum. After about 60 minutes the final vacuum of about 4 mbar was reached. The end of the reaction was shown by the attainment of a defined rotary momentum. The reaction vessel was relaxed with nitrogen, and the reactor emptied through several nozzles over a period of about 60 minutes into a water bath. The product strands were immediately granulated.

The molecular weight and the color of various product batches were determined.

Table 3 gives a survey of the values determined.

Example 15 (Comparison Example)

In an apparatus in analogy to Example 14, the same amount of terephthalic and isophthalic acid as well as ethylene glycol, tetramethylammonium hydroxide, and cobalt acetate tetrahydrate were placed as in Example 14. After the esterification was complete, under a slight vacuum 20 g Pural (hydrotalcite with about 60 percent magnesium) were added. The addition of phosphoric acid was not performed. The liquid phase polycondensation was performed and ended in the manner described in Example 14.

Example 16 (Exemplified Embodiment)

In an apparatus analogous to Example 14, a polycondensation was performed under the same conditions and with the same additives as in Example 15, but without isophthalic acid. Along with the hydrotalcite Pural (20 g), 80 g Irganox 1425 (phosphoric acid ester-based stabilizer from Ciba Geigy) was added to the reaction mixture.

Table 3 contains characteristic values for individual granulate fractions.

Example 17 (Exemplified Embodiment)

Analogous to Example 16, but with the quantity of isophthalic acid given in Example 14, 20 g Pural, and 20 g Irganox 1425.

Characteristic values of the granulate fractions are contained in Table 3.

Example 18 (Exemplified Embodiment)

Analogous to Example 17, but with 20 g Pural and 40 g Irganox 1425.

The characteristic values determined for individual product fractions are summarized in Table 3.

Example 19 (Comparison Example)

Analogous to Example 17, but with 20 g Pural and 40 g Irgafos 168.

Characteristic values of the granulate fractions are contained in Table 3

Example 20 (Exemplified Embodiment)

Analogous to Example 17, but with 20 g Pural and 40 g Irganox PEPQ.

20

Table 3. Characteristic values of various polyester fractions as a function of the catalyst-stabilizer system used.

Experiment	Product fraction no.	Catalyst	Catalyst concentration (ppm)	Stabilizer	Stabilizer concentration (ppm)	Intrinsic viscosity (dl/g)	a - IV (dl/g)	B* color number	a* color number
Example 14 (comparison example)	1 4	Antimony triacetate	640			0.69 0.655	0.035	1.08 3.2	1.12
Example 15 (comparison example)	1 4	Hydrotalcite	250			0.7051 0.6113	0.093	0.53 5.35	4.82
Example 16 (exemplified embodiment)	1 6	Hydrotalcite	250	Irganox 1425	1000	0.6463 0.6251	0.021	-4.61 -2.11	2.5
Example 17 (exemplified embodiment)	1 5	Hydrotalcite	250	Irganox 1425	250	0.674 0.606	0.068	-0.31 3.42	3.73
Example 18 (exemplified embodiment)	1 5	Hydrotalcite	250	Irganox 1425	500	0.683 0.637	0.046	-2.54 0.66	3.2
Example 19 (comparison example*)	1 5	Hydrotalcite	250	Irgafos 168	500	0.6848 0.6118	0.073	1.98 3.81	1.83
Example 20 (exemplified embodiment)	1 5	Hydrotalcite	250	Irganox PEPQ	500	0.672 0.624	0.048	-2.32 0.71	3.03

*Given as "exemplified embodiment" in text.

Tables 2 and 3 illustrate the advantages of hydrotalcites as catalysts for polycondensation reactions. Hydrotalcites at substantially lower concentrations have the same catalytic effectiveness as conventional polycondensation catalysts such as antimony compounds. In combination with the excellent food compatibility, with this new class of polycondensation catalysts an excellent alternative is provided to the currently commercially utilized catalytically active compounds.

The combination hydrotalcite/phosphoric acid ester or phosphorous acid ester permits the synthesis of polyesters with a very high thermal stability. The molecular weight breakdown during processing listed in Table 3 is more favorable than in the case of the polyesters produced under antimony catalysis.

In addition, the products are characterized by a low color tint.

The combination hydrotalcite/phosphoric acid ester or phosphorous acid ester can also be used for the synthesis of other polyesters and for insertion of other monomers into polyalkylene terephthalate

CLAIMS

1. Catalyst systems for polycondensation reactions, characterized in that they are untreated or calcinated hydrotalcite-analogous derivatives of the general formula



5 wherein M(II): divalent metals, M(III): trivalent metals, and A: anions, alone or in combination with phosphorus compounds that contain at least one hydrolyzable phosphorus-oxygen bond.

2. Catalyst systems for polycondensation reactions in accordance with Claim 1, characterized in that M(II) is Mg or Zn or Ni or Cu or Fe(II) or Co.

10 3. Catalyst systems for polycondensation reactions according to Claims 1 or 2, characterized in that M(III) is Al or Fe(III).

4. Catalyst systems for polycondensation reactions according to any of Claims 1 to 3, characterized in that A are carbonates, titanlys or borates.

5. Catalyst systems for polycondensation reactions according to any of Claims 1 to 15 4, characterized in that the calcination of the hydrotalcite-analogous compounds is carried out at temperatures of 200°C to 800°C, preferably at 400°C to 650°C.

6. Catalyst systems for polycondensation reactions in accordance with any of Claims 1 to 5, characterized in that the polycondensation is carried out with the catalysts under vacuum in liquid phase at temperatures of 230°C to 280°C and in solid phase at temperatures 20 of 170 to 240°C.

7. Catalyst systems for polycondensation reactions in accordance with any of Claims 1 through 6, characterized in that the particle sizes of the hydrotalcites used are in the range of 0.1 to 50 µm, preferably 0.5 to 5 µm.

8. Catalyst systems for polycondensation reactions in accordance with Claim 1, 25 characterized in that as the phosphorus compounds, phosphoric acid esters or esters of phosphorous acid are used.

9. Catalyst systems for polycondensation reactions in accordance with Claim 8, characterized in that the catalyst system is used in the proportion, hydrotalcite to phosphorus compound, of 1:0.5 to 1:4, preferably of 1:1 to 1:2.

30 10. A polycondensation product made using a catalyst as described in any of Claims 1 through 9 characterized in that the product is substantially free of heavy metals.

11.A polycondensation product as in Claim 10 further characterized in that the product is suitable for use in bottles, sheets, films or fibers.

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/US 00/33386

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G63/82 C08G85/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 721 305 A (ESHUIS, JOHAN JAN W. ET AL) 24 February 1998 (1998-02-24) abstract; example 1	1-4, 6, 7, 10
A	CAVANI F ET AL: "HYDROTALCITE-TYPE ANIONIC CLAYS: PREPARATION, PROPERTIES AND APPLICATIONS" CATALYSIS TODAY, NL, AMSTERDAM, vol. 11, 1991, pages 173-301, XP000537043 cited in the application page 175 page 213 -page 215	1-5
A	EP 0 172 636 A (WAKO PURE CHEM IND LTD ; TAKEDA CHEMICAL INDUSTRIES LTD (JP)) 26 February 1986 (1986-02-26) claims 9, 11; example 1; table 1	1, 10, 11
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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